On the Variation of the Resistance of Selenium with the Voltage.

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That the conductivity of selenium depends not only upon the illumination but also upon the voltage applied to it was discovered in 1875 by W. G. Adams,[*] and the fact that the selenium preparation examined by Adams had a positive temperature coefficient of resistance made it very improbable that the effect was due to Joulean heat.

G. M. Minchin,[†] using aluminium electrodes, found that the conductivity increased nearly fourfold on increasing the voltage from 2 to 12 volts, and that it was approximately proportional to the voltage.

J. Luterbacher,[‡] in the course of a special study of this "potential effect" ("Spannungseffekt"), found that it is greater for direct currents than for alternating currents of the same energy, that the curve exhibiting the resistance in terms of the voltage is (approximately) parabolic, and that the potential effect cannot be explained by Joulean heat.

F. C. Brown[§] studied the potential effect in a Ruhmer "cell" and a Giltay "cell," and found that the conductivity varies by an amount which in the Ruhmer "cell" is almost proportional to the voltage, while in the Giltay "cell" the variation decreases as the voltage is increased.

C. Ries,[||] using carbon filament electrodes embedded in slate, obtained increases in the conductivity of selenium ranging from 5 to 50 per cent. on increasing the voltage from 0·4 to 4 volts, but the figures given are insufficient to determine the relation between voltage and conductivity. Some further work by the same author is dealt with below.

The present work was undertaken with the object of discovering the relation between voltage and conductivity, and of throwing some further light on the nature of the potential effect.

It is necessary to prefix some definitions.

The Selenium Bridges.—The term "selenium cell" should be restricted, according to Minchin, to the electrolytic cells in which the incident light produces an E.M.F., and not a change of resistance. Such real cells were devised by Sabine in 1878, and improved forms were used by Minchin for the electrical measurement of starlight.* Those selenium preparations, on the other hand, in which the light is used to effect a change in the resistance, Minchin very appropriately calls "selenium bridges," and I propose to adopt this term for all such preparations.

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[*] 'Roy. Soc. Proc.,' 1875, vol. 23, p. 535.

[†] 'Roy. Soc. Proc.,' 1908, A, vol. 81, p. 9.

[‡] 'Ann. der Physik,' 1910, vol. 33, p. 1392.

[§] 'Phys. Rev.,' July, 1911, vol. 33, p. 1.

[||] 'Physikal. Zeitschr.,' July 1, 1911, vol. 12, p. 529.

The Potential Effect.—In all dry selenium bridges, an increase of voltage always produces an increase in the electrical conductivity. This, for reasons which will presently appear, is best expressed as a diminution of resistance. If R_0 is the resistance of a selenium bridge at an infinitesimal voltage, and R_V its resistance at a voltage V, then $(R_0-R_V)/R_0$ is the "potential effect" on the resistance of the bridge in question, or, shortly, the "potential effect." (This must be distinguished from what may be called the "photo-voltaic effect" in electrolytic selenium cells, or the production of an E.M.F. by light. The literal translation of "Spannungseffekt" = "tension effect" is obviously open to misinterpretation, and "voltage effect" is perhaps too suggestive of the "Volta effect" of contact electrification.)

The Coefficient of the Potential Effect.—The main result of the present work is to show that *the potential effect is proportional to the logarithm of the voltage,* in all selenium bridges having graphite electrodes, and for all voltages above 1 volt. This is expressed by the equation

$$\frac{R_1-R_V}{R_1} = F \log V,$$

where R_1 is the resistance at 1 volt and F is a constant for a given bridge under the same conditions as to temperature, illumination, and fatigue.

Method.—Some 70 different selenium bridges were prepared, some of the Shelford-Bidwell type, but most of them by a new method as follows:—Square plates of a highly-insulating unglazed porcelain, 5 cm. wide and 3 mm. thick, were coated on one face with soft graphite. This face was then divided into two separate conducting portions as shown in fig. 1, the to-and-fro separating line being drawn with a diamond. The plate so prepared then received a coating of selenium, either by spreading molten selenium over it with a glass or iron spatula, or by exposing it to a current of selenium vapour. After cooling rapidly, the selenium was sensitised in the usual way by prolonged exposure to a temperature of 200° C.

Three different varieties of stick selenium were used, one of them obtained from Kahlbaum, Berlin, and two others of unknown origin. No special purification was attempted, but as the results did not vary systematically from one specimen to another, nor with the mode of preparation, the conclusions of this paper are not likely to be affected by whatever slight impurities the selenium contained.

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* 'Roy. Soc. Proc.,' 1895, vol. 58, p. 142; and 1896, vol. 59, p. 231.

A few bridges were also prepared by coating the porcelain with a thin layer of selenium in the first instance, and then drawing on the annealed selenium a pattern of thick pencil lines interlaced as above. These bridges had a high resistance, combined, as a rule, with a high sensitiveness to light. But the potential effect showed no marked variation from that observed in the first type.

The lowest temperature used was that of liquid oxygen (−182° C.) and the highest 100° C. All the bridges examined had a negative temperature coefficient of resistance at ordinary temperatures.

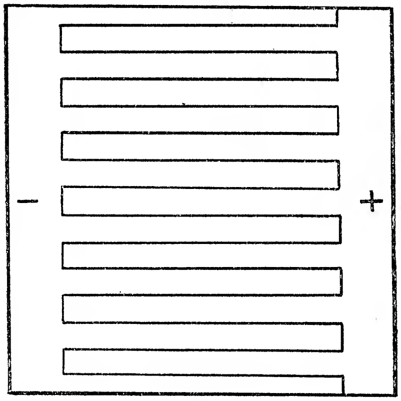

Fig. 1.

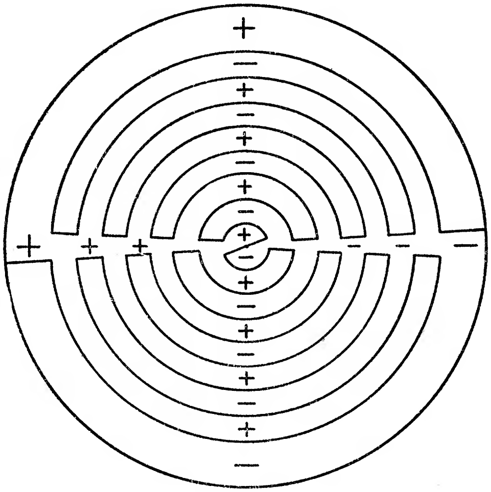

Fig. 2.

In addition to the graphite-selenium bridges, a platinum-selenium bridge, purchased from Presser, Berlin, was studied. It has a circular active surface 4·5 cm. in diameter. From an inspection of this bridge it appears that platinum is deposited upon an insulating surface, and circular concentric lines are ruled in it as shown in the diagram (fig. 2). Selenium is then spread over the whole surface. In the actual bridge there are 40 circles 0·5 mm. apart.

Measurements.—A Wheatstone bridge arrangement is unsuitable, as the voltage applied to the selenium is not necessarily proportional to the voltage used. A substitution method was therefore used throughout. The bridge under examination was put in circuit with a battery and an Ayrton-Mather moving-coil mirror galvanometer giving 6 mm. of a deflection per microampère on a scale 1 m. away. (For measuring the smallest currents, a Broca galvanometer giving a deflection of 4 mm. for 10^{-9} ampère was substituted.) The scales of both galvanometers were carefully calibrated.

The voltage was applied for one minute and then reversed. Readings were taken after one minute in each direction. The two readings were, as a rule, sensibly the same if the bridge had been carefully dried and was protected from moisture, by varnishing or otherwise. The reversal not only tests for polarisation, but enables the bridge to assume the resistance appropriate to the voltage—a point to be borne in mind when testing the voltage law above set forth.

A set of manganin resistances was then substituted for the selenium bridge. The set consisted of 10 coils of 0·1 megohm each, 10 of 0·01 megohm each, and 10 of 0·001 megohm each. The resistance was adjusted to the nearest 1000 ohms, so as to approach as closely as possible to the mean reading for the selenium bridge.

The deflections obtained with the manganin and the selenium respectively (corrected, if necessary, for scale error) were then taken as inversely proportional to their respective resistances.

E.M.F.'s up to 20 volts were obtained from Clark cells, Daniell cells, or small accumulators, whose E.M.F. was compared with that of a Clark cell. Higher voltages were obtained from a set of accumulators capable of yielding up to 800 volts in steps of 20 volts. In using the latter, the voltage was controlled by means of a set of three Kelvin electrostatic voltmeters arranged in parallel across the terminals.

Results.—The logarithmic law was found to hold in *all* the bridges examined, and was, in one instance, verified for a voltage as high as 220. Fig. 3 shows a typical set of readings obtained with the Presser bridge (No. 1) without reversing the current. It will be seen that the resistance oscillates in small jerks about the straight line representing the logarithmic law. These jerks are smoothed out by one or more reversals. The resistance in this case is governed by the relation

$$\begin{aligned} R_V &= (225{,}000 - 38{,}000 \log_{10} V) \text{ ohms} \\ &= 225{,}000\,(1 - 0{\cdot}169 \log_{10} V) \text{ ohms.} \end{aligned}$$

The factor 0·169 appearing in the brackets is the "coefficient of the voltage effect," denoted above by F.

Another set of results, obtained with the Presser bridge after further repose in the dark, is embodied in the following table.

V.	log V.	Δ log V.	R_V.	ΔR.	ΔR/Δ log V.
1·43	0·155	—	252,500	—	—
4·73	0·675	0·519	230,000	22,500	43,300
9·46	0·976	0·820	217,000	35,500	43,300
14·19	1·152	0·996	209,500	43,000	43,200

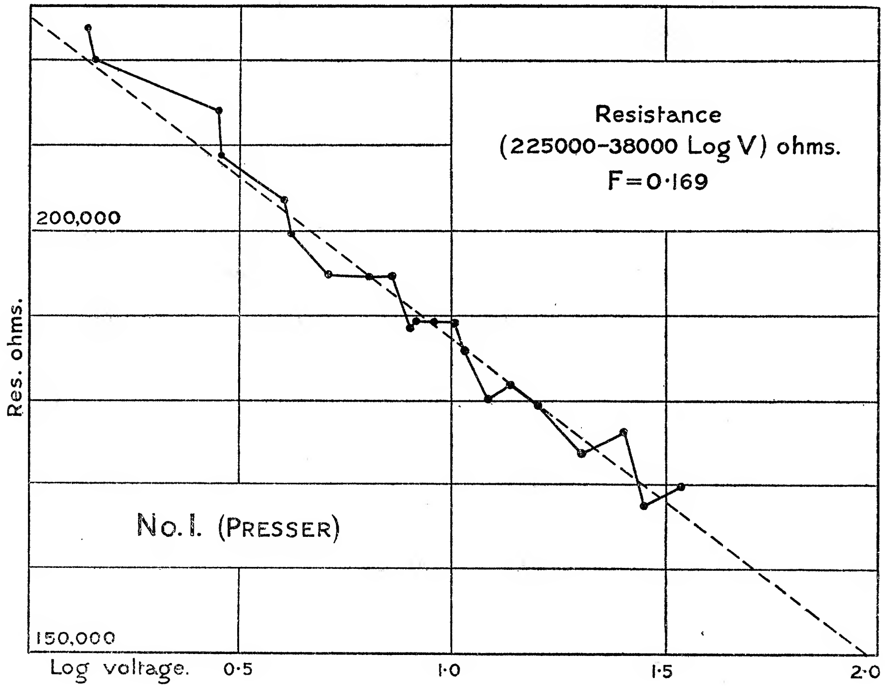

Fig. 3.

The coefficient F is calculated from any two values of the resistance by means of the formula

$$F = \frac{R_V - R_v}{R_V \log v - R_v \log V},$$

where V and v are the two voltages and R_V and R_v the corresponding resistances. The mean value of F from the above table is 0·167.

After a fortnight's repose, the same Presser bridge showed a resistance as high as 339,000 ohms at 1 volt, and a decrease of 56,350 ohms for $\Delta \log V = 1$. This gives $F = 0·167$, as before.

When illuminated by an incandescent gas lamp giving an intensity of 16 metre-candles, the Presser bridge showed a resistance governed by the relation $R_V = (80,500 - 12,500 \log V)$ ohms, which gives $F = 0·155$. From this it was at first thought that F is diminished by white light, but subsequent experience showed that it is sometimes increased.

It may also be stated here that there was no systematic difference between white light and monochromatic light. Thus, a bridge covered with two plates of ruby glass behaves, as far as the potential effect is concerned, as if it were illuminated with white light containing about the same amount of red light As the potential effect occurs also in forms of selenium which are quite insensitive to light, and even in a solid selenium stick, no special study was made of the colour or even the intensity of the light used, the object being merely to test the validity of the logarithmic law for various kinds and intensities of illumination taken at random. And the result was in each case a confirmation of that law.

A selenium-graphite bridge (No. 2), made by smearing selenium over graphite, was examined in darkness, in diffused daylight, in gaslight, and in sunlight; also in liquid air, at 13° C., and at 44° C. Its resistance at 1 volt ranged from 16,000 to 32,000 ohms. The constant F had a mean value of 0·318. It was 0·278 in the dark at 44° C., 0·385 in sunlight at 13° C., and 0·344 in liquid air and dull daylight. The effect of liquid air was to double its resistance while immersed, and to produce a subsequent gradual increase of the resistance to about three times its original amount. This may be connected with the fact that a selenium stick, immersed in liquid air, becomes very brittle and friable.

The behaviour of a bridge (No. 3) similarly made is shown by fig. 4. The resistance R_1 ranged from 39,600 to 8200. The letters indicate the separate series of measurements. The values of F are given by the following table:—

a. Dark	0·278	*e.* Dark	0·290
b. 12 metre-candles	0·274	*f.* Dark	0·276
c. Dark	0·283	*g.* Dark	0·271
d. Dark	0·272	*h.* 12 metre-candles	0·281

The mean value of F is 0·278. If it were the same for all the series, the lines would all intersect in the axis of abscissæ at a point representing 4000 volts.

Curve *j* shows the gradual inception of the potential effect below 1 volt.

Another bridge, which I shall call No. 4, was made by tracing pencil lines on selenium. Its resistance at 1 volt varied very widely, even in the dark. The extreme values were 8·15 megohms and 1·64 megohms in the dark, the former after prolonged repose. The corresponding values of F were 0·190 and 0·232. In sunlight R_1 was 188,000 ohms, and F was 0·157. In spite of these considerable variations of F from one series of measurements to another, the logarithmic law applied very rigidly to any given series, the maximum deviation from it being 0·3 per cent. This is specially valuable inasmuch as the voltage varied from 1 to 100 volts. (For the very high resistances a method of comparative deflections had to be used.)

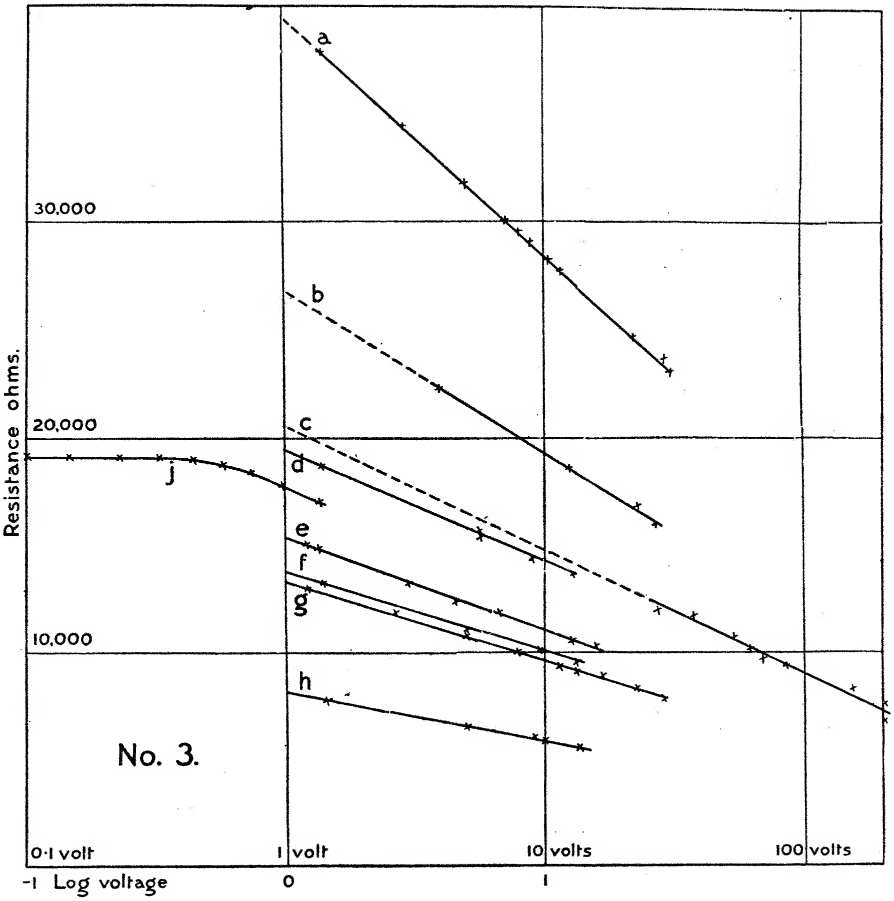

FIG. 4.

No. 5 was a single selenium line between two graphite lines, the gap being 0·5 mm. wide, and the selenium 0·1 mm. thick. The following table gives the values of R₁ (in megohms) and F for six different series of measurements, the highest voltage being 24 volts :—

	R_1.	F.		R_1.	F.
a. At 15° C., dark	3·7	0·33	*d.* At −180° C., daylight	12·2	0·35
b. At 15° C., daylight ...	1·95	0·41	*e.* At −180° C., long daylight	11·2	0·34
c. At −180° C., daylight	20·8	0·42	*f.* At −180° C., long dark......	23·4	0·34

It will be seen that, although R_1 varies 1100 per cent., F only varies 27 per cent. from one series to another.

No. 6 was a bridge formed with selenium vapour, deposited on graphite and annealed. Its resistance was only some 3000 ohms. F was 0·190 in the dark, and 0·193 in gaslight (12 m.c.). No. 7 was made by the same process, but had a thinner film, a higher resistance ($R_1 = 512,000$ ohms), and a greater sensitiveness to light. The mean value of F was 0·26.

The above are a few typical results obtained by me, out of a larger number of series of measurements, all of which pointed to the same conclusion: that the reduction of the resistance is, under conditions otherwise constant, proportional to the logarithm of the voltage (above 1 volt). But F may vary considerably (as much as 30 per cent.) in the same bridge under different conditions of illumination, temperature, and fatigue.

Results of other Observers.—The behaviour of the Giltay "cell," studied by Brown,* confirms in general the logarithmic law, whereas the Ruhmer "cell" does not. But the Giltay bridge shows evident traces of polarisation, which are carefully eliminated from my measurements, and the cases are therefore not comparable.

A Ruhmer bridge also figures in Luterbacher's work,† and on plotting R against log V (abscissæ), a curve is obtained having a very perceptible concavity towards the axis of abscissæ. On the other hand, the figures given for a bridge of the Shelford-Bidwell pattern (p. 1406) under 15, 30, 45, 60, and 125 volts show a satisfactory agreement with the logarithmic law.

I have had no opportunity of examining a Ruhmer bridge, and cannot form any opinion as to the circumstances which cause its deviation from the logarithmic law. But it is evident that bridges made with metallic wires are less likely to yield simple relations than bridges made with carbon, which has no chemical action on selenium.

Quite recently, Ries‡ has carried out a special investigation of the potential effect in selenium and antimonite, without, however, discovering any simple relation between voltage and resistance. The potential effect was observed in a selenium bridge having a positive ("metallic") temperature coefficient of resistance, and Joulean heat is therefore excluded as a cause. The effect is extremely small (F = about 0·03) between 2 and 12 volts, but appears to obey the logarithmic law. At 55 volts and 110 volts the resistance falls very considerably, probably owing to the heating of the support, which was embedded in paraffin. The support was presumably slate, as in Ries's previous experiments, but no information is given on this important point.

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* *Loc. cit.*, p. 21.

† *Loc. cit.*, p. 1400.

‡ 'Ann. der Physik,' December, 1911, vol. 36, p. 1055.

Theoretical.—The strongest argument against the possibility of the potential effect being due to Joulean heat advanced by Luterbacher is that a direct current and an alternating current of the same heating power produce very different potential effects, the D.C. effect being about three times the A.C. effect. But it can also be eliminated by calculating the Joulean heat from the current and resistance, and the rise of temperature from these and the surface and emissivity of the wire. The rise of temperature θ is given by the equation

$$\theta = \frac{0{\cdot}239\,\mathrm{V}^2}{h\mathrm{AR}_0\,(1-\alpha\theta)} = \frac{0{\cdot}239\,\mathrm{V}^2}{h\mathrm{AR}_0}\left(1+\frac{\alpha\,0{\cdot}239\,\mathrm{V}^2}{h\mathrm{AR}_0}\right), \text{ approximately,}$$

where V is the voltage, h the emissivity, A the area, α the temperature coefficient of resistance, and R_0 the resistance at 0° C. under V volts. According to Glazebrook, Bousfield, and Smith,* h in metallic wires ranges from 0·037 to 0·088 cal. per sec. cm.^{2} deg. If it were 0·03 in the Presser bridge, then the rise of temperature at 10 volts in the dark would be 0·0002° C., whereas it would require a rise of some 5° C. to account for the observed 14 per cent. reduction of the resistance. Calculations with regard to other bridges show a similar disproportion, so that Joulean heat is excluded as a cause, unless the emissivity of selenium is 10,000 times smaller than that of metals. Control experiments showed that it cannot in any case be more than 100 times smaller.

This was confirmed by determining the resistance of a pencil line drawn on porcelain under various voltages. The resistance at 1 volt was 66,000 ohms. Exposure to 10 volts produced no measurable change in the resistance, even when prolonged for half an hour.

In the absence of a thermal explanation it becomes necessary to look for some other hypothesis. Luterbacher's "negative polarisation" is hardly adequate, as such a polarisation would itself be difficult to explain. Brown's interesting hypothesis of chemical instability is open to Ries's objection that all chemical processes are linked to definite temperatures, whereas both the sensitiveness and the potential effect in selenium are nearly the same in liquid air as at ordinary temperatures. Ries's sketch of an electronic theory seems the most promising line of investigation, and it may not be very wide of the mark if we compare the conductivity of selenium to that of a gas, due to ionisation by collision modified by a subsequent recombination of the ions.

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[*] 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 541.

In the present uncertainty with regard to the mechanism of conduction in solids it would be premature to attempt a theory of the potential effect on these lines. But, on the other hand, the simple relation between voltage and resistance specified above may furnish some guidance in a future choice among theories of conduction.

In conclusion, I have to thank Prof. Poynting for offering me ample facilities in conducting this investigation, and Prof. T. Turner for some valuable hints regarding the distillation of metals and the treatment of thin conducting films.

The Volatility of Metals of the Platinum Group.

By Sir William Crookes, O.M., For. Sec. R.S.

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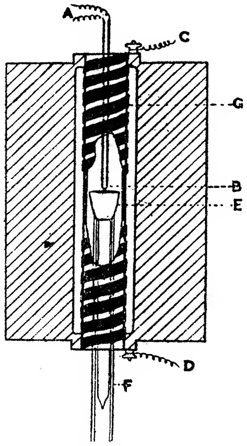
For the last two years I have been using an electric furnace, and some facts which came under my notice on the occasion of a breakdown of the heating arrangement led me to suspect that platinum was not so entirely fixed at temperatures well below its melting-point as has been universally accepted by chemists and physicists.

The electric resistance furnace used (fig. 1) is on the Heraeus system. It consists of a highly refractory porcelain tube, around which is coiled a ribbon of platinum foil, 11 mm. wide, 2·8 metres long, and 0·01 mm. thick,



A, Wires from thermo-junction.
B, Platinum platinum-rhodium junction.
C, D, Terminals of platinum strip.
E, Crucible.
F, Porcelain supporting tube.
G, Platinum strip.

Fig. 1.